Test Material: Dicamba

MRID: 49888501

Title: Field Volatility of Dicamba Formulation MON 119096 Following a Pre-Emerge Application Under Field Conditions in the Southeastern USA

EPA PC Code: 128931

OCSPP Guideline: 835.8100

For CDM Smith

Primary Reviewer: Richard Lester

Signature: Richard R Lester

Date: 7/28/16

Secondary Reviewer: Dan Hunt

Signature: Dan Hunt

Date: 7/28/16

QC/QA Manager: Joan Gaidos

Signature: Joan G

Date: 7/28/16

Field Volatility of Dicamba

Report: MRID 49888501. Jacobson, B., Urbanczyk-Wochniak, E., Mueth, M.G., Riter, L.S., Sall, E.D., Honegger, J., South, S., Carver, L. 2016. Field Volatility of Dicamba Formulation MON 119096 Following a Pre-Emerge Application Under Field Conditions in the Southeastern USA. Unpublished study performed by Waterborne Environmental, Inc., Leesburg, Virginia; Monsanto Company, St. Louis, Missouri; and Agvise Laboratories, Northwood, North Dakota. Study sponsored by Monsanto Company, St. Louis, Missouri. Monsanto Study No.: WBE-2015-0221; Waterborne Study NO.: 666.11. Study initiation April 30, 2015, and completion March 30, 2016 (p. 7).

Document No.: MRID 49888501

Guideline: OCSPP 835.8100

Statements: This study was conducted according to the USEPA FIFRA Good Laboratory Practice (GLP) Standards (40 CFR Part 160), with the following exceptions:

Field Phase:

1) Test site information such as estimation of slope, depth to water table elevation, and GPS coordinates.
2) Study weather data.
3) Pesticide and crop histories for the test plots.
4) Soil information provided by the USDA Natural Resource Conservation Service (NRCS).
5) Test plot preparation prior to application.

Signed and dated Data Confidentiality, GLP Compliance, Quality Assurance, and Authenticity Certification statements were provided (pp. 2-5).

Classification: This study is acceptable. The minimum fetch required for use of the aerodynamic method was not satisfied for all samplers. An independent laboratory method validation was not conducted.

PC Code: 128931

Reviewer: William P. Eckel, Ph.D. **Signature:** William P. Eckel
Senior Science Advisor, ERB6 **Date:** 10/11/2016

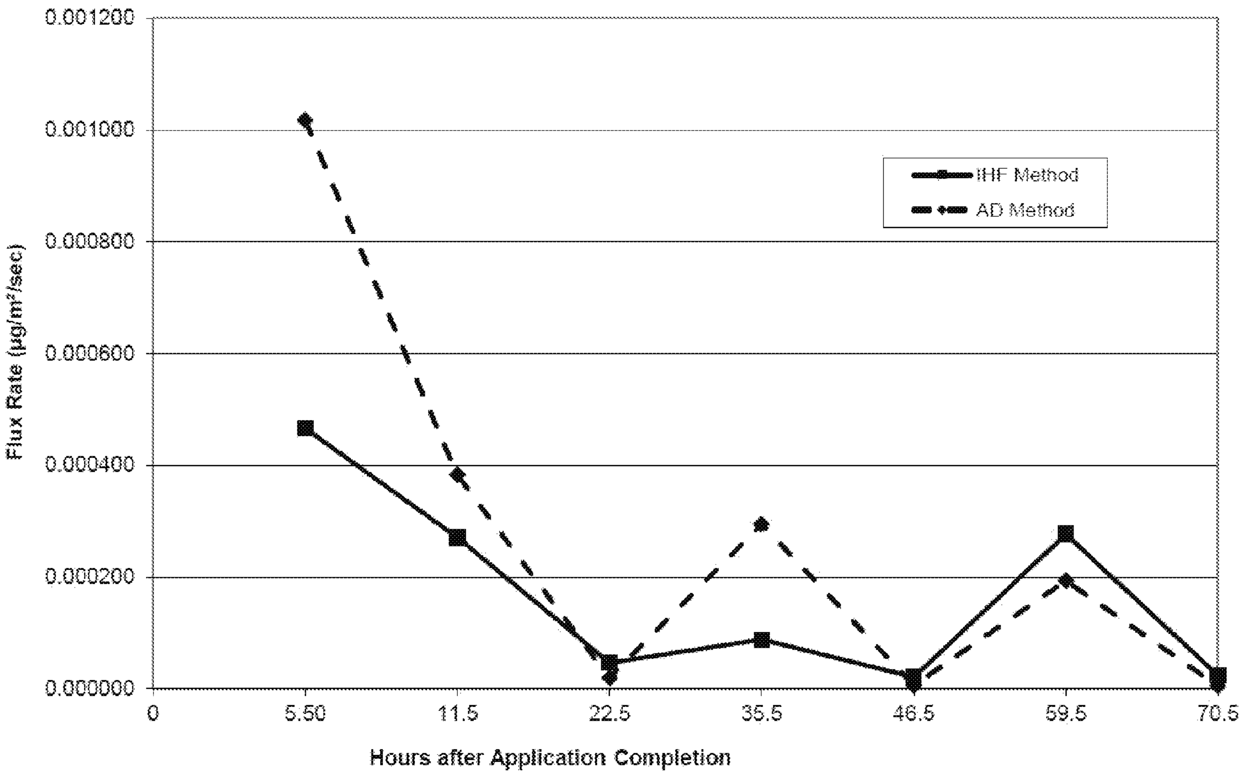
Executive Summary:

Field volatilization of dicamba, formulation MON 119096, a dicamba diglycolamine salt formulation containing 350 g dicamba acid equivalent (a.e.)/L applied in a spray solution containing 0.25% of the non-ionic surfactant Induce®, was examined from a bare plot at one site in Tift County, Georgia. The site where the study was conducted was near Chula, Georgia. The experiment at this site (Site 1/Plot 1) was conducted for approximately three days. The nominal application rate in the plot was 1.0 lb a.e./A (1.121 kg/ha).

Under field conditions at Site 1/Plot 1 based on calculations using the Integrated Horizontal Flux method, dicamba in the MON 119096 formulation had a peak volatile flux rate of 0.000466 $\mu g/m^2 \cdot s$ accounting for 0.008% of the applied observed 0 – 5.5 hours post-application. By the end of the study, a total of 0.03% of dicamba volatilized and was lost from the field after application. Other secondary peak volatile flux rates of 0.000088 $\mu g/m^2 \cdot s$ and 0.000276 $\mu g/m^2 \cdot s$ occurred at 22.5 to 35.5 and 46.5 to 59.5 hours post-application, respectively. Higher flux rates were observed during the first day after application and during the daytime on Days 2 and 3.

Under field conditions at Site 1/Plot 1 based on calculations using the Aerodynamic Flux method, dicamba in the MON 119096 formulation had a peak volatile flux rate of 0.00102 $\mu g/m^2 \cdot s$ accounting for 0.018% of the applied observed 0 to 5.5 hours post-application. By the end of the study, a total of 0.05% of dicamba volatilized and was lost from the field after application. Other secondary peak volatile flux rates of 0.000294 $\mu g/m^2 \cdot s$ and 0.000193 $\mu g/m^2 \cdot s$ occurred at 22.5 to 35.5 and 46.5 to 59.5 hours post-application, respectively. Higher flux rates were observed during the first day after application and during the daytime sampling on Days 2 and 3.

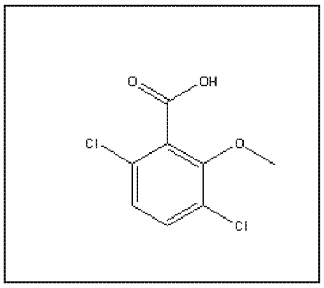
Figure 1. Dicamba Flux Rates



I. Materials and Methods

A. Materials

1. Test Material



Product Name: MON 119096 (p. 17)
Formulation Type: Liquid
CAS #: 104040-79-1 (dicamba diglycolamine salt)
Storage stability: Stability of the active ingredient dicamba in the test substance MON 119096 has previously been demonstrated for 14 days at 55°C and for a related formulation one year under heated warehouse conditions (Appendix 5, p. 88).

2. Storage Conditions

The test substance was shipped by Monsanto Company under ambient conditions on April 28, 2015 and received by Southeastern Ag Research, Inc. (SEAgRes) in Chula, Georgia on April 30, 2015. Upon receipt, the test substance was logged in and stored in a pesticide storage area at ambient temperatures ranging from approximately 66 to 73°F prior to the application (p. 17).

B. Study Design

1. Site Description

The test site was located near Chula, Georgia in Tift County (pp. 17-18). A 3.4 acre (1.37 ha) plot was located in a larger field of bare soil. The plot dimensions were 384 ft x 384 ft (117m x 117m). The soil type of the plot was classified as a Tifton sandy loam, a very deep, well drained, moderately slowly permeable soil on interfluves that formed in loamy marine sediments. The taxonomic class of the Tifton series is – fine-loamy, kaolinitic, thermic Plinthic Kandiudults (Order – Ultisols, Suborder – Udults). The crops on this site for the previous three years were cotton (2012), cotton (2013), and peanuts (2014; Table 2, p. 37). No herbicides containing dicamba had been used on the site for the last three years, although a number of other cotton and peanut herbicides, fungicides, and insecticides were used. The elevation of the site was approximately 370 feet above sea level, and the slope in the test area was estimated to be approximately 2%.

2. Application Details

Application rate(s): The target application rate was 1.0 lb a.e./A (1.121 kg/ha) (p. 19). Based on application monitoring samples in the treated area, the measured application rate (±RSD) was 113 ± 23% of the target application rate (p. 27; Table 7, p. 42). All nozzles were calibrated and pass times were within 2% of the target pass time (pp. 27-28).

Irrigation and Water Seal(s): No irrigation water was used.

Tarp Applications: Tarps were not used.

Application Equipment: A tractor-mounted boom sprayer was used for the broadcast application of dicamba formulation MON 119096 to the treated plot (p. 19). The spray boom was fitted with sixteen Turbo Teejet Induction (TTI 04) nozzles and 50 mesh screens (Table 4, p. 39). The nozzles were spaced 18 inches apart, providing a 24-foot swath width. The boom height was set approximately 18 inches above the soil. The sprayer was equipped with an 80 gallon tank, and a roller pump (PTO driven) was used to pressurize the system and provide agitation (recirculation).

Equipment Calibration Procedures: The sprayer output prior to application was calibrated using water and the spray from each nozzle was collected for 20 seconds in three separate runs (p. 19). The boom pressure was set at approximately 27-28 psi for the calibration trial and test substance application. The calibrated sprayer output for the application was calculated to be 13.5 GPA (Table 4, p. 39). The target sprayer speed was 9.98 feet/sec or 6.80 mph.

Application Regime: The application rates and methods used in the study are summarized in **Table 1**. The adjuvant Induce® (0.25% v/v) was added to the spray tank of the test substance (p. 19).

Table 1. Summary of application methods and rates for MON 119096

Field	Application Method	Time of Application (Date and Start Time)	Amount Dicamba Applied (lbs)	Area Treated (acres)	Calculated Application Rate (lb ae/acre)	Reported Application Rate (lb ae/acre)
1	Broadcast Spray	5/5/2015 08:09	3.4[1]	3.4	1.0	0.999[1]* 1.13[1]**

Data obtained from pp. 19, 27-28; and Table 5, p. 40.
[1] Not reported in the MRID. Data obtained from the registrant-prepared study profile for MRID 49888501.
*Based on sprayer pass timing
**Based on analysis of deposition in the spray area (113% of the target 1 lb ae/acre application rate; p. 27).

Application Scheduling: Critical events of the study in relation to the application period are provided in **Table 2**.

Table 2. Summary of MON 119096 application and monitoring schedule

Field/Plot	Treated Acres	Application Period	Initial Air/Flux Monitoring Period	Water Sealing Period	Tarp Covering Period
Field 1 /Plot 1	3.4	05/05/15 between 08:09 – 8:30	05/05/15 between 8:30 – 14:00	Not Applicable	Not Applicable

Data obtained from pp. 18-19, 20-21 and Table 4-6, pp. 40-41.

3. Soil Properties

Soil properties measured before the study are provided in **Table 3**.

Table 3. Summary of soil properties for fields/plots

Field	Sampling Depth	USDA Soil Textural Classification	USGS Soil Series	WRB Soil Taxonomic Classification	Bulk Density (g/cm^3)	Soil Composition
1	0– 6 inches	Sand	Tifton loamy sand	Fine-loamy, kaolinitic, thermic Plinthic Kandiudults (Order – Ultisols, Suborder – Udults)	1.45	% Organic Matter = 0.53% % Sand = 90% % Silt = 6% % Clay = 4%

Data obtained from p. 18 and Table 3, p. 38.

Figure 2 presents a plot of the soil surface temperature measured 1 mm below the soil surface during the time of the study (Appendix 1, pp. 59-63). Figure 3 presents a plot of the volumetric water content (VWC) as fraction of total soil volume at a depth of 2 inches (Appendix 1, pp. 59-63). Note that the VWC measurement is a relative measurement since the probe was not calibrated to the specific soil and the test site.

Figure 2. Soil Temperature at the Soil Surface (1 mm Depth) after Application

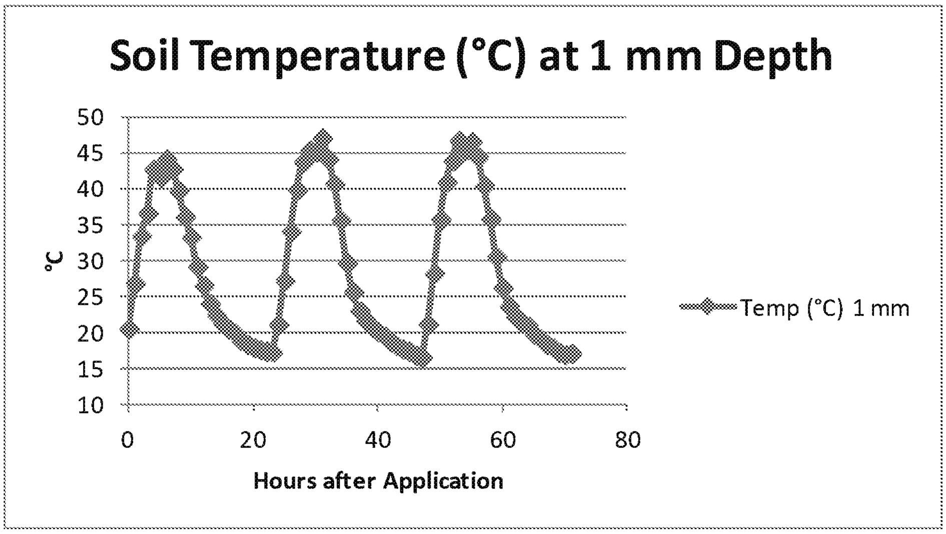


Figure reported by the registrant in the registrant-prepared study profile for MRID 49888501.

Figure 3. Soil Volumetric Water Content after Application

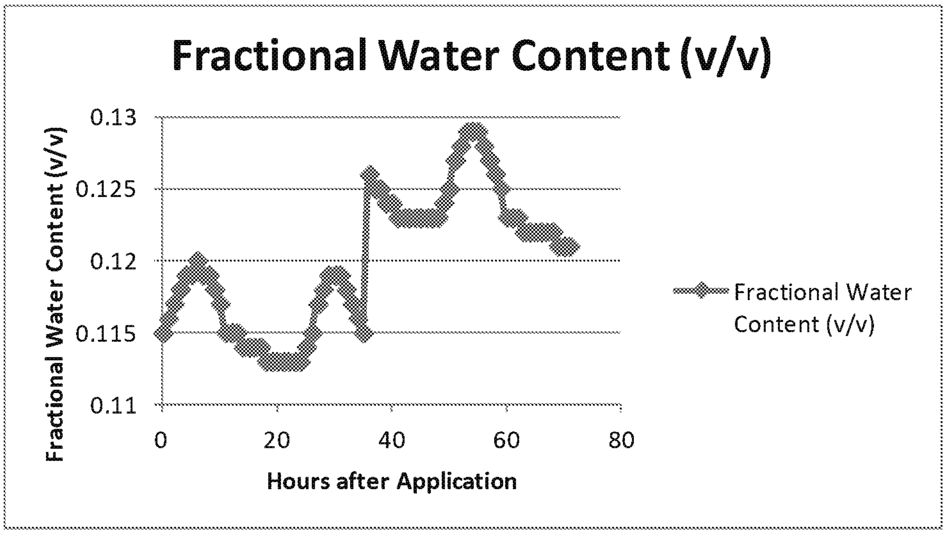


Figure reported by the registrant in the registrant-prepared study profile for MRID 49888501.

4. Meteorological Sampling

Air temperature, precipitation, relative humidity, solar radiation, wind speed, wind direction, soil temperature (1 mm and 2 and 6 inches deep) and reference evapotranspiration, were recorded at the test site using an on-site weather station (p. 18). A summary of hourly and daily climatological data including air temperature (max/min/avg), relative humidity (max/min/avg), ETo, wind speed (max/min/avg), average wind direction, solar radiation, soil temperature (max/min/avg), volumetric water content, and precipitation for the duration of the field volatility sampling is presented in Appendix 1 (pp. 52-63) of the report.

One meteorological station was established about 950 feet east of the plot so that a good representation of the wind pattern of the test plot was achieved (p. 20; Figure 3, p. 48). The station monitored air temperature (using air temperature sensors and radiation shields), and wind speed and wind direction (using sonic anemometers) located at approximately 0.33, 0.55, 0.90 and 1.5 m above the soil surface. Each parameter was measured every second, and the data were summarized every minute and every hour. The hourly wind speed and direction data for each monitoring height is summarized in Appendix 2 (pp. 64.69) of the report. The hourly air temperature data for each monitoring height is summarized in Appendix 3 (pp. 70-75) of the report. The temperature, wind speed, and wind direction at each sampling height summarized on a per minute basis is provided in the Raw Met Data worksheet in the Excel spreadsheets embedded in Attachment 2 of this document.

Details of the sensor heights and the meteorological parameters for which data were collected are illustrated in Table 4. The location of the meteorological equipment for the plot is shown in Attachment 3.

Table 4. Summary of meteorological parameters measured in the field

Field	Minimum Fetch* (m)	Parameter	Monitoring heights (m)	Averaging Period
1	64.8 (58.6)[1]**	Wind speed/Wind direction	Height 0.33, Height 0.55, Height 0.90, Height 1.5	1 minute
		Ambient air temperature	Height 0.33, Height 0.55, Height 0.90, Height 1.5	1 minute
		Precipitation	Not reported	1 hour
		Evapotranspiration	Not reported	1 hour
		Relative humidity	Not reported	1 hour
		Solar radiation	Not reported	1 hour
		Soil temperature	Depth 1 mm, Depth 2 in, Depth 6 in	1 hour
		Soil moisture	Depth 1 mm, Depth 2 in, Depth 6 in	1 hour

Data obtained from p. 18 and Appendices 1-3, pp. 52-75 of the study report.

[1] Not reported in the MRID. Data obtained from the registrant-prepared study profile for MRID 49888501.

* Value indicated is the minimum average fetch for a sampling period. Values on a per minute basis are calculated in the spreadsheets provided in Attachment 2.

**Value in parentheses is from registrant submitted report MRID 49888501. In this report mean fetch for a sampling period is calculated using the resultant wind direction over the sampling period rather than calculating a fetch value for each minute of the sampling period and then taking the mean of those values.

5. Air Sampling

Off-field samples were collected at a height of 1.5 m during the application period (5/5/2015; from 07:55 to 08:31) from eight locations around the test plot (15 m from the edge of the plot; p. 20; Table 6, p. 41; Figure 3, p. 48). Off-field samples were used to determine flux during the application period via the Indirect Flux Method.

The on-field air profile monitoring station in the plot consisted of air sampling pumps mounted on a sampling mast located at the approximate center of the plot (p. 20). Five sample locations (heights) were established on the sample mast at approximately 0.15, 0.33, 0.55, 0.90 and 1.5 m above the soil surface. All air samples for a specific time increment were used for the regression analysis for that increment unless samples were disqualified by breakage or other defined cause. For each sampling time increment, a mass rate of chemical transfer per unit surface area (flux rate) was calculated. Two pre-application (PA) samples were collected at the 0.15 m height near the air monitoring location (center of plot) in the treated plot on May 4, 2015 prior to the start of the application on the following day (Table 6, p. 41). Pre-application samples were collected from 8:04 until 14:20 on May 4.

6. Sample Handling and Storage Stability

Upon collection, the air sampling tubes were immediately placed in an ice chest with ice packs until they were transported to the field cooperator's facility freezer (p. 21). Transit stability samples were prepared/spiked by Monsanto Company, and then shipped frozen to the field site then stored and shipped in the same manner as the actual field samples. A set of air sampling tubes to be exposed in the field were prepared/spiked by Monsanto Company, and then shipped frozen to the field site (pp. 21-22). At the field site, these samples were removed from frozen storage, allowed to reach ambient temperature then exposed to an air flow then placed in frozen storage along with the other field samples.

All samples were later shipped overnight via Federal Express in insulated containers with dry ice to Monsanto Company for analysis (p. 22). The samples were received frozen and were maintained frozen except when a sample was being prepared for extraction. Samples were then stored in a continuously monitored freezer set at approximately -20 °C until analysis (pp. 22-23). All PUF samples in this study were extracted and analyzed within a period of less than 14 days after collection (Appendix 5, p. 89).

Stability of dicamba on PUF sample collectors has been demonstrated in a concurrent stability study (Appendix 5, p. 89; Appendix 6, p. 156). Samples were prepared by fortifying polyurethane foam (PUF) air sampling traps separately with dicamba at a concentration of 0.003 µg /PUF. Samples were removed from frozen storage and analyzed at intervals of 0, 7, 15, 55 and 78 days. The estimated degradation of dicamba was calculated using a statistical regression model. The statistical analysis of the change in measured concentration over time showed no statistically significant change in dicamba over the course of 78 days. Dicamba is therefore considered stable on PUF sample collectors under frozen storage conditions for at least a period of 78 days.

7. Analytical Methodology

- Sampling Procedure and Trapping Material: Dicamba was monitored using glass vapor collection tubes containing polyurethane foam (PUF) sorbent (SKC Inc. Catalog No. 226-92) and SKC® (Model Number 224-52) personal air sampling pumps (p. 21). The vapor collection tubes were attached to a pump using Tygon® tubing. The flow for each sample was calibrated for each sample period using a Bios International Dry-Cal model DC-L12K. The flow was set to approximately 3 L per minute.

- Extraction method: The PUF samples were transferred from the air sampling glass tube to a 50 mL conical tube and extracted by shaking for 30 minutes (1200 cycles per minute) using methanol containing stable-labeled internal standard (p. 23; Appendix 5, pp. 115-116). An aliquot of the supernatant was filtered, evaporated, reconstituted in 25% methanol in water and then dicamba was quantitated using LC-MS/MS with electrospray ionization in negative ion mode (Appendix 5, pp. 118-119).

- Method validation (Including LOD and LOQ): Method ME-1902-01 was validated by assaying 9 replicates each of samples fortified at 0.3 (LOQ), 3 and 60 ng/PUF (p. 23; Appendix 5, pp. 124-125). Capability of dilution was demonstrated using 3 replicate samples fortified at 600 ng/PUF. Validation assessments demonstrated accuracy within 70-120% and precision ≤20% RSD at all fortification levels tested. The specificity of the method was demonstrated through the analysis of control matrices. The limit of quantitation (LOQ) of dicamba was 0.3 ng/PUF determined during method development (Appendix 5, p. 107). The LOD was determined to be 0.065 ng/PUF through statistical determinations on validation data (Appendix 5, pp. 87, 90). Additional method validation performed on Method ME-1902 (same methodology as Method ME-1902-01; Appendix 5, p. 106) also showed acceptable mean recoveries (mean recovery between 70-120% and RSD ≤20%) at fortification levels of 0.30, 3.0, 60, and 600 ng/PUF (Appendix 5, Table 2, p. 95).

- Instrument performance: Calibration curves were linear with 1/x weighting (Appendix 5, p. 90). The working range of the method was from 0.3 to 75 ng/PUF. Extension of the upper range of the method to 750 ng/PUF can be achieved using lower injection volumes, therefore overall the method covered sample concentrations from 0.3 to 750 ng/PUF.

8. Quality Control for Air Sampling

Lab Recovery:	Most laboratory spike recoveries are within the acceptable range of 90-110% following fortification at 0.3, 3, 60, and 600 ng/PUF; however, four of twelve recoveries were outside of the acceptable range, including two of three recoveries at 0.3 ng/PUF (recoveries of 78.5% and 82.8%) and two of three recoveries at 600 ng/PUF (recoveries of 84.2% and 85.0%) (p. 30; Appendix 5, p. 131).
Field blanks:	There was no dicamba measured in the samples collected before application (Table 3, p. 96).
Field Recovery:	Mean recovery of dicamba from field spikes fortified at 3.0, 30.0 and 600 ng/PUF, and following either a 6- or 12-hour weathering period, ranged from 93.6 to 103% (overall recoveries of 82.0 to 114%; pp. 22, 29; Appendix 6, Table 2, pp. 167-168); recoveries were similar across the fortification ranges and weathering conditions. The length of storage was not reported.
Travel Recovery:	Mean recovery of dicamba from transit stability samples fortified at 3.0 and 30.0 ng/PUF was 100% (range from 94.3 to 105%) and 104% (range from 102 to 106%), respectively (Appendix 6, Table 3, p. 169). Transit samples were stored for 16 days prior to extraction, and were stored in the same manner as the test samples (p. 21).

Breakthrough: Samples that were fortified at 600 ng/PUF and exposed in the field for 12 hours had an average recovery of 93.6%. Samples fortified at 30 ng/PUF and exposed for 12 hours had an average recovery of 103%. The highest dicamba amount measured on a PUF (49 ng) was less than 10% of the highest fortification (600 ng) indicating that dicamba loss due to breakthrough did not occur at the dicamba air concentrations present in this study (Appendix 4, pp. 77-78; Appendix 6, Table 2, pp. 167-168).

9. Application Verification

To verify the application of the test substance, ten application monitoring devices, pre-labeled pans each containing five Whatman #3 filter papers (12.5 cm in diameter; total area of 614 cm^2) were placed diagonally across the plot area (p. 19). As soon as possible after application the five filter papers in each pan were placed into a pre-labeled 16 oz. plastic bottle, and each bottle was sealed and stored in a portable freezer (while in the field).

Recoveries achieved on extraction and analysis of application monitoring devices were in the range 64 to 157%, with a mean (±RSD) recovery of 113 ± 23% (n=10) (p. 27; Table 7, p. 42). Recoveries achieved on extraction and analysis of laboratory fortification of application monitoring filter papers ranged from 102 to 104% (p. 30).

II. Results and Discussion

A. Empirical Flux Determination Method Description and Applicability

For estimation of flux after application in this study, both the Aerodynamic Method and the Integrated Horizontal Flux Method were used.

Aerodynamic Method

The aerodynamic method, also referred to as the "flux-gradient" method, was one of the two techniques employed for estimating flux rates from the field treated with MON 119096 for this field study given the available data. For the aerodynamic method, a mast was erected in the middle of the treated field, and samples for air concentration measurement were collected at five different heights, 0.15, 0.30, 0.55, 0.90, and 1.5 meters above the soil surface. Likewise, temperature and wind speed data were collected at 0.30, 0.55, 0.90, and 1.5 meters above the soil surface at a weather mast positioned just outside of the spray plot. Log-linear regressions were performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. These relationships were then utilized to calculate input parameters for the equation to estimate flux.

The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the aerodynamic method in particular is the Thornthwaite-Holzman Equation, which is shown in the following expression:

Equation AD-1 $$P = \frac{k^2(\Delta\bar{c})(\Delta\bar{u})}{\phi_m \phi_p [\ln\left(\frac{z_2}{z_1}\right)]^2}$$

where P is the flux in units of µg/m²·s, k is the von Karman's constant (dimensionless ~0.4), $\Delta\bar{c}$ is the vertical gradient pesticide residue concentration in air (regressed) in units of µg/m³ between heights z_{top} and z_{bottom} in units of meters, $\Delta\bar{u}$ is the vertical gradient wind speed (regressed) in units of m/s between heights z_{top} and z_{bottom}, and ϕ_m and ϕ_p are atmospheric momentum and vapor stability correction terms, respectively. The heights z_{top} and z_{bottom} are chosen to fall within the range of the sampler heights deployed in the field test, and, as indicated above, both the air concentration and wind speed values at these two heights are obtained from linear regression equations relating concentration and wind speed to the natural log of vertical height .

Following the conditions expected in the neutrally stable internal boundary layer characterized by an absence of convective (buoyant) mixing but mechanical mixing due to wind shear and frictional drag, a log-linear regression is performed relating the natural logarithm of the sample height to the concentration, temperature, and wind speed. The adjusted values of the concentration, temperature, and wind speed from this regression are incorporated into Equation AD-1 to arrive at Equation AD-2 which is ultimately used to compute the flux.

Equation AD-2 $$Flux = \frac{-(0.42)^2(c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m \phi_p \ln\left(\frac{z_{top}}{z_{bottom}}\right)^2}$$

ϕ_m and ϕ_p are internal boundary layer (IBL)stability correction terms determined according to the value of the Richardson number, R_i, which is calculated as shown in Equation AD-3:

Equation AD-3 $$R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\frac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] * (u_{ztop} - u_{zbottom})^2}$$

where T_{ztop} and $T_{zbottom}$ are the regressed temperatures at the top and bottom of the vertical profile in units of °C.

if $R_i > 0$ (for Stagnant/Stable IBL)
$\phi_m = (1 + 16R_i)^{0.33}$ and $\phi_p = 0.885(1 + 34R_i)^{0.4}$

if $R_i < 0$ (for Convective/Unstable IBL)
$\phi_m = (1 - 16R_i)^{-0.33}$ and $\phi_p = 0.885(1 - 22R_i)^{-0.4}$

Special Comments regarding EPA and Registrant's calculations for the flux estimation by the AD Method

Important special comments relating to the Registrant's use of the AD Method in the present submission are:

1. The original articulation of Equation AD-3 in this template document specified the denominator as the sum of the two bracketed terms, when in fact it should be specified as the product. This has been corrected in the text. The calculation in the EPA spreadsheet embedded with this document did correctly multiply the two terms.

2. While the equations above indicate that the exponent for calculating ϕ_m is -0.33 or +0.33 (depending on the value of Ri), the Excel spreadsheet for the aerodynamic method provided with this template uses the value +/- 0.30483 for this exponent. For the flux values provided by the Registrant in Table 5, the exponent value of +/- 0.33 has been used.

3. The flux values provided in Table 5 as Registrant values use 0.40 as the von Karman's constant (see, for example, Majewski, et. al., 1990) while the Aerodynamic Method calculations in the example spreadsheet use a value of 0.42.

4. The Registrant has corrected two cell assignment errors that are present in the example Excel spreadsheet for the aerodynamic method.

    i. In the Conc. Summary worksheet, the regression formulas in Columns I, J, and K, Row 3, reference the sampler heights specified by the User in Columns C through F, Row 2. However, the reference to the Row 2 Heights is lost when Row 3 of Columns I, J, and K, is copied down to other rows (sampling periods). This is because the reference to the Row 2 Heights is not specified as an absolute reference.

       Thus, as an example, the formula in Column J, Row 3 of the Conc. Summary worksheet should be "=INTERCEPT(C3:F3,LN(C$2:F$2))", wherein the addition of the "$" designation in the Row 2 references ensures that the reference to sampler heights always points to Row 2 when the formula is copied down to subsequent sampling periods. This correction has been applied to Columns I, J, and K in the Conc. Summary worksheet.

    ii. Similar referencing corrections have been applied to the wind and temperature regression formulas in Columns I, J, and K of the Met Data Summary worksheet to ensure that the appropriate row is specified when accessing the sampler height data.

5. The minimum fetch requirement that the fetch is 100 times the highest height of the air sampler for this method to be valid was not satisfied for the samplers positioned at 0.90 and 1.5 meter above the soil surface for any of the sampling times; however, this treated

plot was bare soil, and the separation of the plot from obstacles such as trees that would impact air flow was indeed sufficient to establish excellent linearity for the regression of temperature and wind speed with the natural log of sampler height. Also, flux and total mass loss values are in very good agreement between the aerodynamic flux method and the Integrated Horizontal Flux Method. This agreement indicates that the fetch was of sufficient length for the aerodynamic method to be valid for this plot.

Integrated Horizontal Flux Method

The integrated horizontal flux method, also referred to as the "mass balance" method, was used as the second technique employed for estimating flux rates from the field treated with MON 119096 for this field study given the available data. For the integrated horizontal flux method, a mast was erected in the middle of the treated field, and samples for air concentration measurement were collected at five different heights, 0.15, 0.30, 0.55, 0.90, and 1.5 meters above the soil surface. Likewise, temperature and wind speed data were collected at 0.30, 0.55, 0.90, and 1.5 meters above the soil surface at a weather mast positioned just outside of the spray plot. A log-linear regression was performed relating the natural logarithm of the sample height to the air concentration and wind speed following the log linear relationships for the atmospheric boundary layer. Subsequent wind speeds and air concentrations required as inputs to the equation used to estimate flux are then determined from these regression equations.

The methods to estimate flux and related equations are presented in Majewski et al., 1990. The equation for estimating flux using the integrated horizontal flux (IHF) method in particular is given by the following expression:

Equation IHF-1 $$P = \frac{1}{x}\int_{Z_0}^{Z_p} \bar{c}\bar{u}\,dz$$

where P is the volatile flux in units of $\mu g/m^2 \cdot s$, $\bar{c}$ is the average pesticide residue concentration in units of $\mu g/m^3$ at height Z in units of meters, $\bar{u}$ is the average wind speed in units of m/s at height Z, x is the fetch of the air trajectory blowing across the field in units of meters for the sampling period in question, Z_0 is the aerodynamic surface roughness length in units of meters, Z_p is the height of the plume top (the height at which air concentration falls to zero) in units of meters, and dz is the depth of an incremental layer in units of meters.

The text and the embedded spreadsheet that accompany this template document describe a numerical evaluation of the integral in Equation IHF-1 by application of the trapezoidal integration technique. In this case Equation IHF-1is modified to the summation shown in Equation IHF-2, below (Yates, 1996):

Equation IHF-2 $$P = \frac{1}{x}\sum_{Z_0}^{Z_P} (A * Ln(z) + B) * (C * Ln(z) + D)dz$$

where A is the slope of the wind speed regression line by ln(z), B is the intercept of the wind speed regression line by ln(z), C is the slope of the concentration regression by ln(z), D is the intercept of the concentration regression by ln(z), and z is the height above ground level. The embedded spreadsheet (and the Registrant) interprets Z_0 as the aerodynamic surface roughness, i.e., the point at which the wind speed profile extrapolates to zero velocity. In turn, the material supplied with this template document calculates Z_p, the height of the concentration plume, using Equation IHF-3, below.

Equation IHF-3 $$Z_P = \exp\left[\frac{(0.1 - D)}{C}\right]$$

However, the Registrant is not familiar with the derivation behind this equation for evaluating Z_p and uses instead the alternative (but similar) equations IHF-6 and IHF-7, as described in Comment 2 of the following Special Comments section.

Special Comments regarding EPA and Registrant's methods and calculations

Important special comments relating to the Registrant's use of the IHF Method in the present submission are:

1. The linear equations relating the wind speed and air concentration to the natural log of the height, Z, afford an analytical solution to the integral specified in Equation IHF-1. The Registrant utilizes this analytical solution to evaluate Equation IHF-1, rather than the numerical integration through application of the Trapazoidal Rule, represented in Equation IHF-2 and used in the provided embedded IHF spreadsheet.

   Thus, if

   Equation IHF-4 $$P = \frac{1}{x}\int_{Z0}^{Zp}(C\ln(z) + D)(A\ln(z) + B)dz$$

   Then

   Equation IHF-5

   $$P = \left[\frac{A \cdot C}{x}(z(\ln(z))^2 - 2z\ln(z) + 2z) + \frac{(A \cdot D + C \cdot B)}{x}(z\ln(z) - z) + \frac{(B \cdot D)}{x}z\right]_{Z0}^{Zp}$$

   In which the symbols have the same meanings as those described for Equation IHF-2, above.

2. Regarding Z_p, the upper limit of the indicated integration –

The Registrant has not seen reference to an equation for calculating the height of the concentration plume that includes the subtraction of D from 0.1 in the numerator of the bracketed fraction seen in Equation IHF-3. Instead, the Registrant calculates the plume height as that value of Z at which the air concentration falls to zero. This is found by specifying a zero concentration in the regressed linear equation relating air concentration to the natural log of the height, Z, as seen in Equation IHF-6 below. Solving Equation IHF-6 for Z_p yields Equation IHF-7. It is this value for Z_p that the Registrant uses for the upper limit of the integral of Equation IHF-1. These Z_p are also entered as Z_{max} in the IHF Flux Analysis worksheet, Column N.

Equation IHF-6 $$0 = C^*\ln(Z_P) + D$$

Equation IHF-7 $$Z_p = \exp\left[\frac{-D}{C}\right]$$

3. <u>Regarding Z_0, the lower limit of the indicated integration</u> –

   As specified in the example calculations provided with this template, the Registrant uses the Aerodynamic Surface Roughness, termed Z_0, as the lower limit for the integral of Equation IHF-1. Z_0 is the height at which the wind speed profile extrapolates to zero. In the present case this is found by specifying a zero wind speed in the regressed linear equation relating wind speed to the natural log of the height, Z, as seen in Equation IHF-8 below. Solving Equation IHF-8 for Z_0 yields Equation IHF-9. It is this value for Z_0 (for each sampling period) that the Registrant uses for the lower limit of the integral of Equation IHF-1. These Z_0 are also the values entered as the Aerodynamic Surface Roughness in the IHF Flux Analysis worksheet, column M.

   Equation IHF-8 $$0 = A^*\ln(Z_0) + B$$

   Equation IHF-9 $$Z_0 = \exp\left[\frac{-B}{A}\right]$$

4. As in the aerodynamic method spreadsheet, the regression equations in the Conc. Summary and the Met Data Summary worksheets contain non-absolute cell assignment errors when referencing the user specified sampling heights. See Comment 4 in the Aerodynamic Method Section above. These errors have been corrected by specifying the sampling height references as absolute row addresses.

5. The minimum fetch requirement of 20 meters for this method to be valid was satisfied at all times. The treated field was a bare soil field with an estimated slope of about 2% . The maximum surface roughness was therefore very much less than 0.1 meters, thus this method validity criterion was met.

6. Regarding the value of x, the average fetch distance for a given sampling period –

The Registrant and the example IHF spreadsheet embedded in this template document approach the calculation of x in slightly different manners.

For any given sampling period (Event), the Registrant calculates the average fetch by first calculating the wind speed weighted average wind angle over the course of the Event time window. This average velocity weighted wind angle is then used in a single calculation to calculate the average fetch. The embedded IHF spreadsheet, on the other hand, calculates average fetch by first calculating the fetch associated with the minute by minute wind angle data compiled in the Raw Met Data worksheet and then averages those results over the time period of the sampling event. In more concise terms, for each Event the Registrant calculates fetch from the wind speed weighted average of the raw wind direction data, while the embedded spreadsheet calculates fetch as the average of the raw fetch data.

The distinctions described above lead to minor differences in the fetch values used in IHF-5 when calculating flux by the IHF method.

B. Temporal Flux Profile

The flux as determined by the registrant as reported in MRID 49888501 and as determined by using the Excel spreadsheet provided by EPA in the Study Profile Template for the Field Volatility study (http://www.epa.gov/pesticide-registration/study-profile-templates#fate) for each sampling period after the application is provided in **Table 5**. Note that the Excel spreadsheet used for the flux calculation has been reviewed as described in Section A above to ensure that cell assignments are correct for each calculation.

Table 5. Field volatilization flux rates of MON 119096 obtained in Georgia study, 1 lb a.e./A application rate

Sampling Period	Date/ Time	Sampling Duration (hours)	Flux Estimate			
			EPA Spreadsheet ($\mu gm^{-2}sec^{-1}$)	Registrant Report ($\mu gm^{-2}sec^{-1}$)	Empirical Flux Determination Method	Notes
Application	05/05/16	0.367	--	0.008079	IF	
1	05/05/15 8:30 – 14:00	5.5	0.001083 0.000420	0.001017 0.000466	AD IHF	
2	05/05/15 14:00 – 20:00	6.0	0.000409 0.000244	0.000382 0.000271	AD IHF	
3	05/05/15 20:00 – 05/06/15 7:00	11	0.000021 0.000042	0.000019 0.000046	AD IHF	
4	05/06/15 7:00 – 20:00	13	0.000314 0.000098	0.000294 0.000088	AD IHF	
5	05/06/15 20:00 – 05/07/15 7:00	11	0.000007 0.000018	0.000006 0.000021	AD IHF	
6	05/07/15 7:00 – 20:00	13	0.000207 0.000256	0.000193 0.000276	AD IHF	
7	05/07/15 20:00 – 05/08/15 7:00	11	0.000005 0.000022	0.000005 0.000023	AD IHF	

Data obtained from Table 6, p. 41 and Tables 8-9, pp. 43-44 in the study report and the accompanying excel spreadsheets.
*Methods legend: AD = Aerodynamic Method, IHF = Integrated Horizontal Flux, IF = Indirect Flux Method.

III. Study Deficiencies and Reviewer's Comments

1. The registrant uses a different approach to calculate Z_p, the top of the concentration plume, than that recommended by EPA when calculating volatilization flux rates using

the Integrated Horizontal Flux method. This results in small differences between flux values calculated in the registrant report and in the accompanying EPA spreadsheets.

2. The minimum fetch required for use of the aerodynamic method was not satisfied for the samplers positioned at 0.90 and 1.5 meters above the soil surface.

3. Analytical method validation was performed, but the method was not independently validated. A method validation study should be completed from an independent laboratory separate from and prior to the analysis of the test samples to verify the analytical methods.

4. The test plot was not irrigated. The study design should include irrigation according to the label requirements.

5. Soil bulk density, soil temperature, soil moisture, and organic matter content were reported at only a single depth of 0-6 inches.

6. A control plot was not established.

IV. References

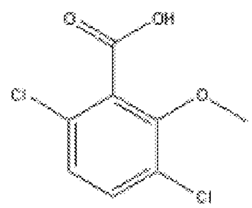
Johnson, B., Barry, T., and Wofford P. 1999. Workbook for Gaussian Modeling Analysis of Air Concentrations Measurements. State of California Environmental Protection Agency, Department of Pesticide Regulation. Sacramento, CA.

Majewski, M.S., Glotfelty, D.E., Kyaw Tha Paw U., Seiber, JN. 1990. A field comparison of several methods for measuring pesticide evaporation rates from soil. Environmental Science and Technology, 24:1490-1497.

Wilson, J.D., and Shum. W.K.N. 1992. A re-examination of the integrated horizontal flux method for estimating volatilisation from circular plots. Agriculture Forest Meteor. Vol 57:281-295.

Yates, S.R., F.F. Ernst, J. Gan, F. Gao, and Yates, M.V. 1996. Methyl Bromide Emissions from a Covered Field: II. Volatilization," Journal of Environmental Quality, 25: 192-202.

Attachment 1: Chemical Names and Structures

Code Name/ Synonym	Chemical Name	Chemical Structure
PARENT		
MON 119096/ Dicamba as the diglycolamine salt	**IUPAC:** 3,6-Dichloro-*o*-anisic acid **CAS:** 3,6-Dichloro-2-methoxybenzoic acid **CAS No.:** 104040-79-1 **Formula:** $C_8H_6Cl_2O_3$ **MW:** 221.04 g/mol **SMILES String:** CLc1ccc(CL)c(OC)c1C(=O)(O)	

ED_005172C_00000915-00020

Attachment 2: Statistics Spreadsheets and Graphs

The electronic spreadsheet files are inserted below for calculations using the Aerodynamic Method and the Integrated Flux Method for determination of the emission rate of dicamba after application in the form of the diglycolamine salt in the formulation MON 119096.

1. Validation spreadsheet for studies following the Aerodynamic Method:

field-volatility-835-81
00-MRID_49888501_

2. Validation spreadsheet for studies following the Integrated Horizontal Flux Method:

field-volatility-835-81
00-MRID_49888501_

Attachment 3: Field Volatility Study Design and Plot Maps

Point	Latitude (°N)	Longitude (°W)
A	31.5741914	-83.59281253
B	31.57314012	-83.59293121
C	31.57303852	-83.5917029
D	31.57408972	-83.59158548
Flux Mast	31.57360986	-83.59223683
Wind Speed Sensors	31.5736725	-83.58867308
Thermocouple Sensors	31.57372527	-83.58867269
Weather Station (not shown)	31.573611	-83.588611

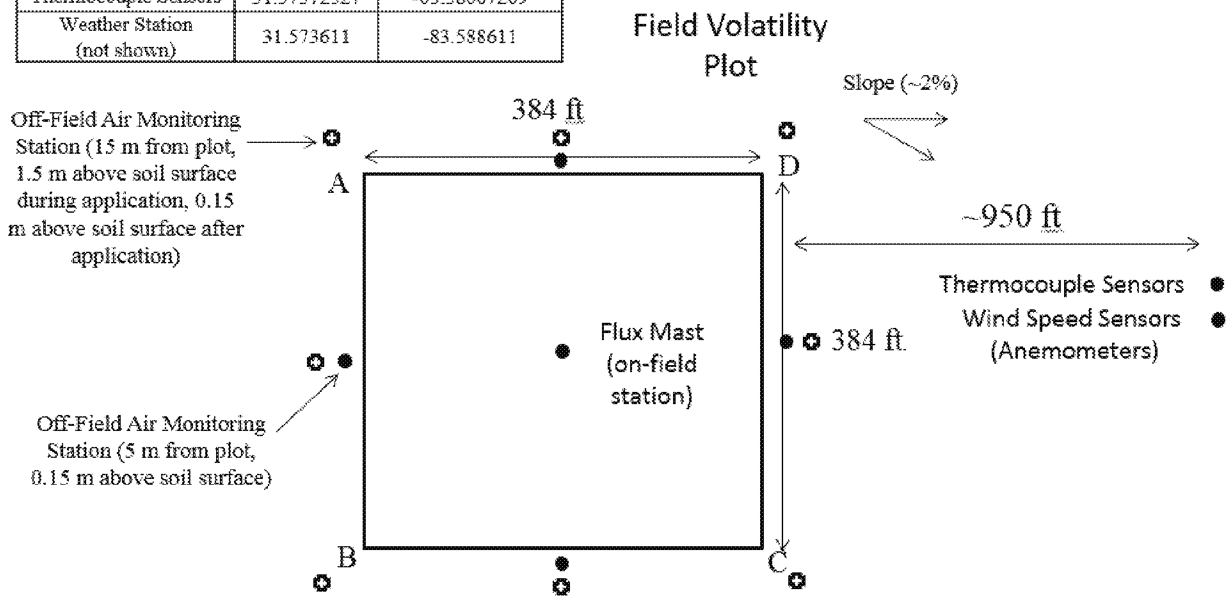


Figure obtained from Figure 3, p. 48, in the study report.

Attachment 4: Calculations and Index of Variables Used in Flux Determination Methods

Aerodynamic Method

Equation x_1 $$Flux = \frac{-(0.42)^2 (c_{ztop} - c_{zbottom})(u_{ztop} - u_{zbottom})}{\phi_m \phi_p \ln\left(\frac{z_{top}}{z_{bottom}}\right)^2}$$

Flux ($\mu g/m^2 s$): volatile flux of pesticide from release source surface
c_{ztop} ($\mu g/m^3$): concentration at the top sampler adjusted according to the regression of concentration vs. ln (height)
$c_{zbottom}$ ($\mu g/m^3$): concentration at the bottom sampler adjusted according to the regression of concentration vs. ln (height)
u_{ztop} (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. ln (height)
$u_{zbottom}$ (m/s): wind speed at the top sampler adjust according to the regression of wind speed vs. ln (height)
ϕ_m and ϕ_p (dimensionless): Internal Boundary Layer (IBL) stability correction terms determined according to the following conditions based on the calculation of the Richardson number, R_i:

Equation x_2 $$R_i = \frac{(9.8)(z_{top} - z_{bottom})(T_{ztop} - T_{zbottom})}{\left[\left(\frac{T_{ztop} + T_{zbottom}}{2}\right) + 273.16\right] * (u_{ztop} - u_{zbottom})^2}$$

where:

T_{ztop}: Temperature at the top sampler adjusted according to the regression of temperature vs. ln (height)
$T_{zbottom}$: Temperature at the bottom sampler adjusted according to the regression of temperature vs. ln (height)
R_i (dimensionless): Richardson Number

if $R_i > 0$ (for Stagnant/Stable IBL)
$$\phi_m = (1+16R_i)^{0.33} \text{ and } \phi_p = 0.885(1+34R_i)^{0.4}$$

if $R_i < 0$ (for Convective/Unstable IBL)
$$\phi_m = (1-16R_i)^{-0.33} \text{ and } \phi_p = 0.885(1-22R_i)^{-0.4}$$

Integrated Horizontal Flux Method

Equation x_3 $$P = \frac{1}{x}\sum_{Z_0}^{Z_P}(A * Ln(z) + B) * (C * Ln(z) + D)dz$$

P ($\mu g/m^2 s$): volatile flux of pesticide from release source surface
z (m): height above ground level
A (s^{-1}): slope of the wind speed regression line by ln(z)
B (m/s): intercept of the wind speed regression line by ln(z)
C ($\mu g/m^4$): slope of the concentration regression by ln(z)
D ($\mu g/m^3$): intercept of the concentration regression by ln(z)
Z_0 (m): aerodynamic surface roughness length of release source surface
Z_p (m): volatile plume top height; calculated from the following equation:

Equation x4

$$Z_P = \exp\left[\frac{(0.1 - D)}{C}\right]$$